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Kinetic Investigation on the Color Striking of Gold Ruby Glass

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Abstract

Gold ruby glass of recipes 71SiO_2, 11CaO, 11Na_2O, 1PbO, 6K_2O (in wt. %) were melted in alumina crucibles at 1500 °C for 2 h with SeO_2 (0-200 ppm) and C (0.1-0.25 wt %) as reducing agents and gold (in flaky form) at 200 ppm as a colorant. Clear glass samples were annealed at 570 °C for 30 minutes. The kinetics of striking mechanism were studied by a UV-Vis spectrophotometer accompanied with a heating stage in order to determine a precise annealing and heat treatment schedule, and to increase the uniformity of the red colour in glass. The glass specimens were heated at 625 °C, 650 °C and 700 °C for 5 – 300 minutes respectively. The investigations on an absorption peak appeared close to the typical ruby colour absorption (530 nm) presented the self-striking capability. Results showed that the potential self-striking glass contained 200 ppm of Au^0, 100 ppm of SeO_2, and 0.20 in wt % of C. The appropriate striking temperature was at 650 °C, and the threshold of the soaking time was 270 minutes.

Keywords: self-striking glass; gold ruby glass;red glass;coloured glass

1. Introduction

Gold ruby glass is a red color glass produced by adding gold carriers to form gold nanoparticles dispersing in the glass matrix. A certain size and shape of gold nanoparticles (AuNPs) can response with electromagnetic field of light and emit the red color by the special optical property of metal nanoparticles called as localize surface plasmon resonance [1]. In typical gold ruby glass production, gold compound such as gold chloride (Au(III)Cl_3), potassium gold chloride ($KAuCl_4$) have been used with reducing agents such as tin oxide (SnO_2) ,tin chloride ($SnCl_2$) in soda lime silicate glasses [2]. This type of gold

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ruby glass needs an additional heat treatment to strike a nucleation and growth process of gold particles with optimum size and shape, therefore a red color is generated. The state of gold in colourless glass can be analyzed by Mössbauer spectroscopy [3, 4] which show that the isomer shift of 1.0 mm/s and a splitting of 6.2 mm/s attributed to Au(I) dissolved in glass matrix. The transformation of Au(I) to metallic gold is reversible. After annealing or secondary heat treatment gold ion Au(I) transformed to metallic gold and a red color is generated

The ruby color of glass shows the absorption peak at 520 nm in the visible wavelength. The larger size of AuNPs exhibit purple and sometimes blue colour while distorted shapes of AuNPs can shift the absorption peak of gold to various wavelengths [5, 6]. Viscosity and temperature are the important factors to determine a nucleation and growth rate of particles which effect to a certain morphology and a size of gold clusters in glass [7]. If a nucleation process can not proceed well regarding to high viscosity in glass, consequently the color cannot be obtained in a thermal treatment. Reducing agents reduce Au(I) in a glass matrix to Au^0 which initiates the nucleation process. Some additives play an important role to increase dissolve rate of gold in glass such as lead [8].

Self-striking glass means the color generation occurred without an additional heat treatment. To produce self-striking gold ruby glass in this study, gold foil which is abundant in Thailand was used as a colorant, selenium oxide and carbon were used as additives [9]. Selenium is very important reducing agent for self-striking gold ruby glass. Actually selenium has been widely used in glass melting for decolorizing purpose. It exists in many forms and shows various colors depending on valence states [5], namely colorless, yellowish brown, and pink. Carbon, in this study was used to control the redox condition of glass.

2. **Experimental**

A base glass in weight percents of $72SiO_2$, 11CaO, $11Na_2O$, 1PbO, $6K_2O$ was selected for this study with the fixed amount of gold i.e., 200 ppm, but various contents of selenium and carbon were selected as shown in Table 1. Glass batches were melted in alumina crucibles at 1500 °C for 2 h. The glasses were then annealed at 570 °C for 30 minutes. The annealing temperature was obtained from the fiber elongation technique and confirmed by the dilatometric measurement as described in other work [9].

Table 1. Glass samples with variation of additives

Glass No.	Amount of additives		
	Au^0 (ppm)	SeO_2(ppm)	C (wt%)
G1	200	200	0.10
G2	200	150	0.15
G3	200	100	0.2
G4	200	50	0.25

In order to find the optimum holding time and temperature to produce a self- striking gold ruby glass, kinetics of color generation of glass samples were investigated by using UV/Vis/NIR spectrophotometer (TRAIX 320, Jobin-Yvon, Edison, N. Y., USA) combined to a heating stage (TS 1500, LINCAM, Great Britain). The glass sample was cut and polished to a thin circle plate with a diameter of 5 mm and 0.5 mm thick, then placing in a chamber of heating stage covered by quartz glass on the top. The heating stage was operated with a heating rate of 5 K/minute and held in various durations, namely 5 – 300 minutes (5 h) at temperatures of 650 °C, 700 °C respectively.

3. Results and Discussion

After the annealing process, glass samples were visually observed. Most of annealed glasses were clear. It could be said from now that when the amount of SeO_2 decreased from 200 ppm and the amount of C increased from 0.1 to 0.25 in wt %, the colors of glasses were not much different. Afterwards, the kinetics of color strikings or color onsets of glasses were investigated, firstly only at two temperature, namely 650 °C and 700 °C. In each temperature, the heating stage combined with a polychromatic UV-Vis spectrophotometer revealed the glass absorption spectral which were measured at the desired holding time. The absorption spectral undertaken at various temperatures and times are presented in Fig. 1, 2, 3 and Fig. 4 for glasses G1, G2, G3, G4, respectively.

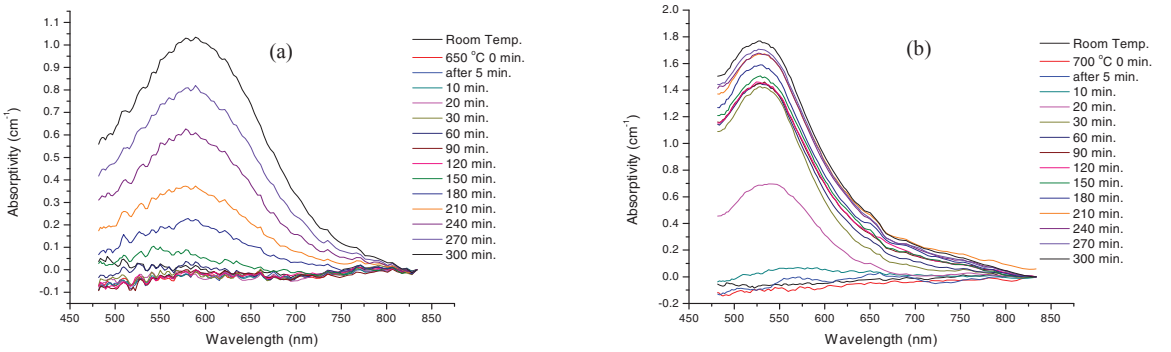

Fig. 1. Absorption peaks of G1 in heating stage at (a) 650 °C and (b) 700 °C

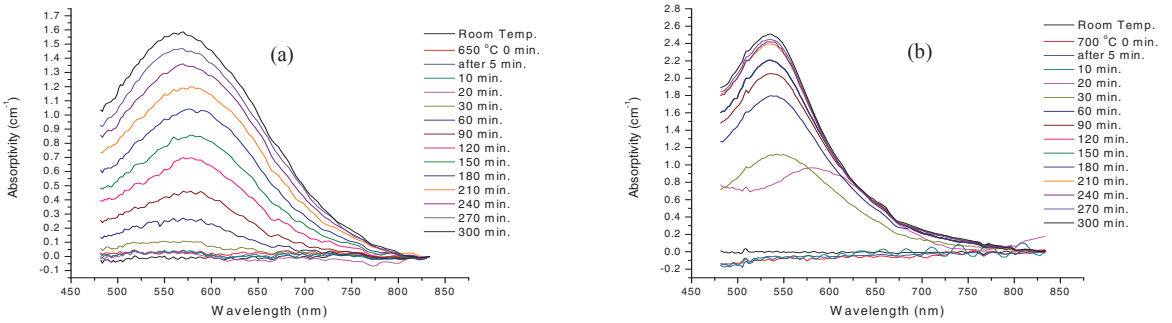

Fig. 2. Absorption peaks of G2 in heating stage at (a) 650 °C and (b) 700 °C

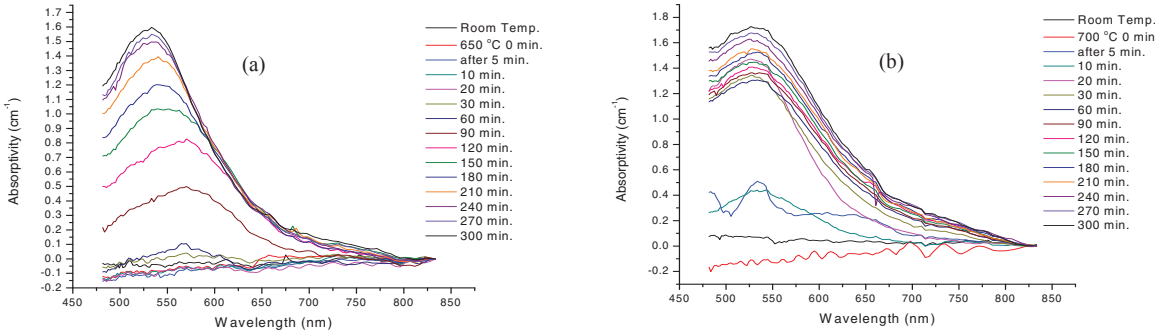

Fig. 3. Absorption peaks of G3 in heating stage at (a) 650 °C and (b) 700 °C

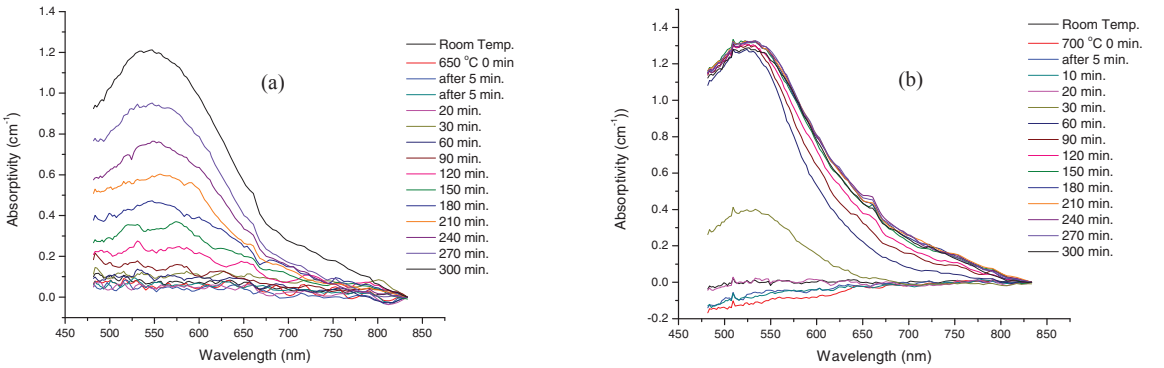

Fig. 4. Absorption peaks of G4 in heating stage at (a) 650 °C and (b) 700 °C

From all figures, it is apparently that at lower temperature 650 °C, only G3 showed red absorption peak of gold at around 530 nm, the others showed the same but at higher temperature which was 700 °C. More kinetic study was done for G3 at the lower temperature 625 °C. Figure 5 illustrates the result.

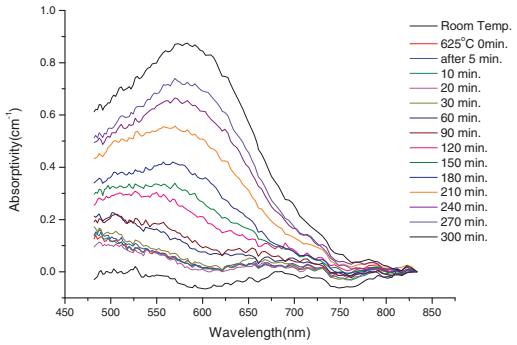

Fig. 5. Absorption peaks of G3 in heating stage at 625 °C

We considered that G3 glass was the best potential in terms of the lowest striking color at 650 °C. Lower temperature at 625 °C was then further studied. But the obtained spectrum in Fig. 5 showed no success in red color generation. The maximum absorption peaks of all glasses are summarized in Table 2.

Table 2. Absorption peaks and color of glass samples

Glass no.	Absorption peaks at 625 °C, nm	Color	Absorption peaks at 650 °C, nm	Color	Absorption peaks at 700 °C, nm	Color
G1	-	-	588	purple	528	red
G2		-	570	purple	535	red
G3	583	purple	533	red	527	red
G4	-	-	547	purple	527	red

At 650 °C, absorption maximum of G3 glass was at 533 nm which is very close to a typical gold ruby glass adsorption at around 530 nm [5, 6]. At this temperature only G3 glass turned into red, the color of G1, G2, and G4 glasses were all purple which was confirmed by the position of the absorption peak that occurred at higher wavelength. When the striking temperature increased to 700 °C, the absorption peaks of ruby color found in G1, G3 and G4 glasses were at 527 nm which were getting closer to 530 nm. At the same temperature, an increase of time will shift the absorption spectra toward higher wavelength due to the growth of AuNPs. Table 3 shows the relation between the absorption and holding time of glass G3

Table 3. Absorption peak of G3 glass at 650 °C with different holding time

Holding time, min	Absorption peak, nm
5	833
10	730
20	833
30	569
60	569
90	569
120	569
150	540
180	540
210	540
240	537
270	533
300	533

At the holding time of 270 minutes, an absorption peak around 530 nm was obtained; this could be the starting period for red color generation.

4. Conclusion

In summary, a self-striking gold ruby glass can be produced if the glass recipe including specific kind and quantity of minor ingredients are optimum. The kinetics study of the striking mechanism done by a heating stage attached with a monochromatic UV-Vis spectrophotometer revealed the gold absorption peak which is between 520 to 530 nm at 650 °C with the holding time at this point, namely 210 minutes at least. This can be later counted as the striking temperature. This kinetics study can be applied for red ruby glass production to select appropriate annealing conditions after forming. However, 210 minutes is

too long that another option by using a higher striking temperature at 700 °C with shorter holding time should take into account. Moreover, further studies should be done to verify these kinetic investigations.

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